Improving the properties of emulsifiable formulation of pesticides in relation to efficacy against pests

II- Efficacy of chlorpyrifos and cypermethrin with surfactants against cotton bollworms and land snails

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ABSTRACT

This study is carried out to evaluate the effect of two non –ionic surfactants on the efficacy of chlorpyrifos, 48 % EC (Pyriban) and cypermethrin, 25 % EC (Sparkil) on both the cotton bollworms and two land snails. The results could be summarized as:

1 – Both polyoxyethylene glycol (PEG) 600 di-oleate and Top Film as local surfactants at concentration of 0.1 % highly reduced the surface tension of water (72.8 dyne cm^{-1}) to 53.17 and 48.08 with the two substances, respectively. These surfactants had HLP value ranged between (8-10) indicating that these emulsifiers gave stable milky dispersion when added to water.

2 - Surface tension value of chlorpyrifos (Pyriban) emulsion (62.64 dyne cm^{-1}) is decreased to 48.7 when tank mixed with PEG 600 di-oleate and to 53.67 with Top Film surfactants. The surface tension values were decreased from 58.05 to 49.6 and 49.13 with cypermethrin (Sparkil) emulsion with the evaluated adjuvant, respectively. The all emulsion treatments passed the emulsion stability tests.

3 - Chlorpyrifos emulsion mixed with PEG 600 di-oleate (0.1 %) significantly increased the efficacy against the cotton bollworms at the recommended rate of insecticide. Same effect was obtained with cypermethrin treatment.

4 – According to a feeding technique using lettuce leaves sprayed with chlorpyrifos or untreated with adjuvants indicated that the toxicity against *Thepa pisana* and *Eubania vermiculta* molluscs was significantly increased along 15 days of treatment.

The emulsifiable concentrates related to certain pesticides may will be more efficient against pests when mixed with surfactants after tank mix to improve absorption and adhesion of the pesticides on the sprayed plants.

INTRODUCTION

It is well known that surfactants are essential for the formulation of most agrochemical products. They have several functions such as emulsifying, solubilizing and wetting. They lower the surface and interfacial tension. These adjuvant can emulsify oils into water as dispersing phase. On the other hand, surfactants and other adjuvants have been used to enhance the biological performance of the pesticide (Schwartz and Perryl; 1949, Oispow; 1964, Foy and Pritchard; 1996, Knowles; 1998 and EL-Shahaat; *et al.*; 2010). Therefore, certain surface active agents and wetting agents may reduce the recommended rates of pesticides decreasing the adverse impact of the toxicants.

This study is carried out to evaluate the influence of non-ionic surfactants on the emulsifiable concentrates of pesticides; chlorpyrifos and cypermethrin, towards their properties when added to the spray tank. Also, the efficacy of the surfactants-pesticids combinations against both the cotton bollworms and two agricultural snails is evaluated.

MATERIALS AND METHODS

1 – Surface-active agents

a - Polyoxyethylene glycol (PEG) 600 di-oleate, as a non-ionic surfactant produced by the Egyptian Co. for Starch, Yeast and detergents.

b – Top Film as an emulsifier chemically unknown composition produced by EL-Help Co. for Agrochemicals and Pesticides, Egypt.

2 - Pesticides

a - Chlorpyrifos, 48 % EC (Pyriban) as a contact organophsphorus insecticide. Its recommended rate of application is 1 L / feddan against the cotton bollworms in Egypt.

b - Cypermethrin, 25 % EC (Sparkil) as a contact pyrethroid insecticide. Its recommended rate in Egypt against the cotton bollworms is 600 cm^3 / feddan.

3 – Physical properties of chlorpyrifos and cypermethrin alone and combined with emulsifiers

a – Surface tension value (dyne cm^{-1}), is determined according to Traub Stalgamometer method (Findely; 1941) using series concentration from 0.02 to 0.10 % in aqueous dilution for each surfactant.

b – Emulsion stability test, is carried out at the field rate of the pesticides alone and combined with each surfactant (0.1 %) modified to WHO Specifications (Anonymous; 1976). Surface tension value, foam volume and either creamy or oily separation were recorded after just emulsification and after ½ hour.

C – Hydrophilic – Lipophilic Balance value (HLP) was determined according to Griffin (1954).

4 – Experiments

A – Field evaluation against cotton bollworms:-

Each experimental plot is sprayed by one insecticide using Knapsak sprayer (20 L-capacity). Three sprays for each insecticide were done and the spraying is carried out after 2 weeks for chlorpyrifos and after 3 weeks for cypermethrin treatments. The insecticide was evaluated at two rates; recommended and 0.75 recommended rates alone and blended with the tested emulsifier (0.1 %). The field experiments were started on 4th Aug., 2008 in cotton field (Giza 70 variety) at Beheira governorate. The evaluated treatments as well as a check treatment were distributed in a complete block randomized design. The inspection of cotton bollworms; *Heliolthis armigera* , *Earias insulana* and *Pectinophora gossypiella* by sampling 100 bolls / plot, was weekly carried out. The % infestation reduction was measured according to Hinderson and Tilton (1955). The obtained results were statistically analyzed according to Steel and Torrie (1980).

B – Evaluating Chlorpyrifos against two terrestrial snails

Lettuce plants were field sprayed by chlorpyrifos, 48 % EC (at 0.5 L/ 200 L water) alone and mixed with one of the tested emulsifier (0.1 %). The efficacy of treatments were laboratory conducted according to feeding technique using lettuce leaves sampled after 1, 3, 5, 7, 10 and 15 days of spray. These sprayed leaves were exposed to two snails. The first one is the brown garden snail; *Eubania vermiculta* while the 2nd one is the small garden snail; *Thepa pisana*. The % mortality values were estimated according Abbot's formula (1925).

RESULTS AND DISCUSSION

The results shown in Table (1) showed that polyoxyethylene glycol 600 di-oleate decrease the water tension surface value with increasing its concentration. The surface tension value decreased to reach a range of 65.1 – 53.2 dyne cm^{-1}. Also, Top Film surfactant gave decreasing the surface tension to a rang of 62.2 – 48.1 dyne cm^{-1}.The two surfactants gave HLP value as (9-10) and (8-10) for the 1st one and 2nd one, respectively. These results indicate that the two surfactants are good to improve the EC formulation of the insecticides.

The data in Table (2) indicate that the surface tension for chlorpyrifos emulsion (62.64 dyne cm^{-1}) was gradually decreased as the polyoxyethylene glycol (PEG) 600 di-oleate increased where it reached to 48.7 dyne cm^{-1} with PEG surfactant concentration of 0.1% while the value is lowered to 53.67 dyne cm^{-1} with Top Film surfactant at the same concentration. On the other hand, the surface tension of cypermethrin emulsion is decreased from 58.5 dyne cm^{-1} to reach to 49.6 and 49.13 dyne cm^{-1} with two tested surfactant at 0.1 % concentration. The two pesticides passed the emulsion stability test without undesirable observations such as foaming and oily or creamy separation.

Results in Tables (3&4) show the residual toxicity of chlorpyrifos and cypermethrin pesticides alone and mixed with PEG surfactant on cotton bollworms. The general mans after 3 sprays show that the residual efficacy of chlorpyrifos gave the highest infestation reduction of cotton bollworms (78.5 %) for the recommended rate of application mixed with PEG 600 di-oleate while the value was 73.87 % with the pesticide alone. The efficacy values were 70.73 and 63.5 with 0.75 recommended rate of the pesticide mixed with surfactant and the evaluated rate mixed with Top Film, respectively. The infestation reduction % values of cotton bollworms were arranged as: cypermethrin at its recommended mixed with PEG 600 di-oleate (84.63) > the insecticide alone at recommended rate (79.33) > the insecticide (0.75 R) + the surfactant (77.63) > the insecticide (0.75 R) alone (67.23).

The results illustrated that the efficacy of the pesticides may be increased when tank-mixed with the suitable emulsifiers. These findings may be attributed to the fact that the emulsifiers can decrease the surface tension or increase the surface activity of the pesticide dilutions. This influence could improve the wettability property of the sprayed plant surfaces and improve the adhesion and spreading of the pesticides. These explanation is agreed with that reported by EL-Sebae and EL-Okda (1972), Valkenburg (1973) and Knnowles (1998).

The efficacy of chlorpyrifos on the small snail garden and brown garden snails are shown in Table (5). The feeding on treated lettuce leaves appeared that mean mortality percentages after 15 days of spray were arranged as chlorpyrifos + PEG 600 di-oleate treatment (57.7) = the pesticide + Top Film (60.48) > chlorpyrifos alone (56.90) for the 1st snail. The obtained results with 2nd snail were (59.21) = (59.24) > (54.42) for the previous treatments, respectively. The increasing the molluscicidal effect of the tested pesticide may be attributed to the increasing the deposits of the pesticide influencing by the surfactants. It is well known that chlorpyrifos was not considered as molluscicide. However, this study just shows the molluscicidal effect related to a pesticide may be increased using some adjuvant such as surfactant. The role of importance of the emulsifiers was previously reported by many investigators (Shwartz and Perry, 1949, Sparr and Brown, 1954 and EL-Okda et al., 1985).

Table (1): Hydrophilic – Lipophilic Balance " HLB", surface tension and surface activity values of two surfactants in aqueous dilutions

Surfactants	Conc. (%)	Surface tension (ϖ) dyne cm^{-1}	Surface activity ($ϖ_0$ - ϖ)* dyne cm^{-1}	HLP values (5gm. Surfactant +95 ml. H_2O)
polyoxyethylene glycol 600 di-oleate	0.02	65.1	7.7	(9-10)
	0.04	64.6	8.2	
	0.06	62.9	9.9	
	0.08	59.5	13.3	
	0.10	53.2	19.6	
Top Film	0.02	62.2	10.6	(8-10)
	0.04	59.1	13.7	
	0.06	57.9	14.9	
	0.08	55.4	17.4	
	0.10	48.1	24.7	

$ϖ_0$: Surface tension value of dist. Water (72.8 dyne cm^{-1} at 25° C)

Table (2): Some physical properties of the emulsions of Pyriban (Chlorpyrifos) and Sparkil (Cypermethrin) at their recommended rates with two surfactants

Pesticide + Emulsifier	Emulsifier conc. (%)	Surface tension dyne cm^{-1}	Emulsion properties: After mixing		½ hr. after mixing	
			Foam (%)	Creamy or oily separation	Foam (%)	Creamy or oily separation
		Pyriban " Chlorpyrifos" 48 % EC"				
Pesticide emulsion	0.00	62.64	0.0	No separation	Nil	2 ml creamy layer at bottom
" + E_1	0.02	62.00	0.0	No separation	Nil	N.S. *
" + E_1	0.04	61.37	0.0	No separation	Nil	N.S.
" + E_1	0.06	58.57	1.0	No separation	Nil	N.S.
" + E_1	0.08	55.12	1.0	No separation	Nil	N.S.
" + E_1	0.10	48.70	1.5	No separation	Nil	N.S.
" + E_2	0.02	62.22	0.0	No separation	Nil	N.S.
" + E_2	0.04	57.89	0.0	No separation	Nil	N.S.
" + E_2	0.06	58.53	0.0	No separation	Nil	N.S.
" + E_2	0.08	56.24	0.0	No separation	Nil	N.S.
" + E_2	0.10	53.67	0.0	No separation	Nil	N.S.
		Sparkil "Cypermethrin, 25 % EC"				
Pesticide emulsion	0.00	58.05	Nil	No separation	Nil	½ ml creamy layer at bottom
" + E_1	0.02	53.29	1.0	No separation	Nil	N.S. *
" + E_1	0.04	50.92	1.5	No separation	Nil	N.S.
" + E_1	0.06	50.21	2.0	No separation	Nil	N.S.
" + E_1	0.08	50.45	3.5	No separation	Nil	N.S.
" + E_1	0.10	49.60	3.7	No separation	Nil	N.S.
" + E_2	0.02	56.21	0.50	No separation	Nil	N.S.
" + E_2	0.04	55.16	0.50	No separation	Nil	N.S.
" + E_2	0.06	53.53	0.75	No separation	Nil	N.S.
" + E_2	0.08	51.45	1.00	No separation	Nil	N.S.
" + E_2	0.10	49.13	2.00	No separation	Nil	N.S.

E_1: Means a polyoxyethylene glycol (600 di-oleate) emulsifier E_2: Means a Top Film emulsifier * N.S. = No eparation

Table (3): Residual toxicity of Pyriban (Chlorpyrifos" 48 % EC) at two rates alone and mixed with a non –ionic emulsifier to bollworms

Chlorpyrifos (48 % EC)	Infestation reduction % 1st Spray 1 week	1st Spray 2 week	1st Spray Mean	2nd Spray 1 week	2nd Spray 2 week	2nd Spray Mean	3rd Spray 1 week	3rd Spray 2 week	3rd Spray Mean	General mean
Pesticide at recommended rate(R)	85.7	66.7	76.2 b	79.3	63.7	71.5 b	71.4	76.3	73.9 b	**73.87 b**
Pesticide (R) + Emulsifier* (0.1%)	88.6	76.7	85.7 a	85.0	67.9	76.5 a	76.7	73.3	75.0 a	**78.50 a**
Pesticide at 0.75 recommended rate	66.77	53.7	60.2 d	66.6	59.7	63.2 c	67.9	66.2	67.1 d	**63.50 d**
Pesticide (0.75 R) + Emulsifier*(0.1%)	6.3	57.8	67.1 c	76.3	52.1	64.2 c	73.9	69.5	71.7 c	**70.73 c**

* The emulsifier is polyoxyethylen glycol 600-Di oleate

Table (4): Residual toxicity of **Sparkil (Cypermethrin, 25 % EC)**at two rates of application to bollworms alone and mixed with a non –ionic emulsifier to bollworm

Cypermethrin (25 % EC)	Infestation reduction % 1st Spray 1 week	1st Spray 2 weeks	1st Spray 3 weeks	1st Spray Mean	2nd Spray 1 week	2nd Spray 2 weeks	2nd Spray 3 weeks	2nd Spray Mean	3rd Spray 1 week	3rd Spray 2 weeks	3rd Spray 3 weeks	3rd Spray Mean	General mean
Pesticide at recommended rate(R)	87.7	77.8	73.3	78.9 b	84.5	81.2	71.4	79.0 b	87.3	82.6	70.4	80.1 b	**79.33 b**
Pesticide (R) + Emulsifier* (0.1%)	92.9	85.7	70.0	82.9 a	93.3	86.7	76.2	85.4 a	94.4	85.0	77.3	85.6 a	**84.63 a**
Pesticide at 0.75 recommended rate	75.0	66.7	50.0	63.9 d	75.0	70.0	64.3	69.8 d	81.7	65.9	56.3	68.0 d	**67.23 d**
Pesticide (0.75 R) + Emulsifier*(0.1%)	78.6	69.7	62.5	70.3 c	78.0	73.3	67.9	73.1 c	83.6	77.3	62.5	74.5 c	**72.63 c**

* The emulsifier is polyoxyethylen glycol 600-Di oleate

Table (5): Residual toxicity of Pyriban (Chlorpyrifos" 48 % EC) pesticides alone and mixed with two emulsifiers to two terrestrial snails

Treatment	Mean mortality percentage *												
	The small garden snail *Thepa pisana*						The brown garden snail *Eubania vermiculta*						General mean
	1 day	3	5	10	15 days	Mean	1 day	3	5	10	15 days	Mean	
Chlorpyrifos	62.5	60.6	60.7	57.2	43.5	56.90 b	57.5	56.6	54.2	49.8	41.6	51.94 b	**54.42 b**
Chlorpyrifos + E_1	63.5	62.1	61.6	60.7	57.7	61.12 a	58.7	58.6	57.6	55.5	56.2	57.30 a	**59.21 a**
Chlorpyrifos + E_2	62.4	61.5	60.5	59.6	58.4	60.48 a	60.2	59.7	59.7	57.8	55.7	58.00 a	**59.24 a**

E_1 & E_2: They are polyoxyethylen glycol 600-Di oleate and top film emulsifiers, respectively

* each values is an average of 5 replicates

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الملخص العربى

تحسين خواص المركزات القابلة للإستحلاب للمبيدات وعلاقة ذلك بالفاعلية ضد الأفات ٢ – فعالية مبيدى كلوربيريفوس وسيبرمثرين خلطا مع بعض المواد النشطة سطحيا ضد ديدان اللوز والقواقع الأرضية

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إجريت هذه الدراسة لتقييم تأثير إثنين من عوامل النشاط السطحى غير الأيونية على فعالية كل من مبيدى كلوربيريفوس 48 % EC (بايريبان) وسيبرمثرين 25 % EC (سباركل) ضد ديدان اللوز فى محصول القطن وتأثير المبيد الأول ضد نوعين من القواقع الأرضية. ويمكن تلخيص النتائج المتحصل عليها كالأتى:-

1 – كل من بولى إيثيلين جليكول 600 داى – أولييت ومادة توب فيلم كل منهما بتركيز (0.1%) تسبب خفضا كبيرا فى قيمة التوتر السطحى للماء من 64.8 داين سم$^{-1}$ إلى 53.17 ، 48.08 على الترتيب للمادتين على الترتيب . أيضا فإن قيمة التوازن الهيدروفيلى – الليبوفيللى تراوحت بين 8 – 10 مما يدل على أن هاتين المادتين تعطى مستحلبا ثابتا عند الخلط مع الماء وهو مستحلب من نوع زيت / ماء.

2 – وجد أن قيمة التوتر السطحى لمستحلب الكلوربيريفوس تنخفض من 62.64 داين سم$^{-1}$ (بدون أى مادة نشطة سطحيا) إلى 48.7 داين سم$^{-1}$ أثناء الخلط الحقلى مع الماء فى وجود مادة بولى أوكسى إيثيلين 600 داى – أولييت وإلى 53.67 داين سم$^{-1}$ مع مادة توب فيلم. ومع مبيد سيبرمثرين فإن قيمة التوتر السطحى للمستحلب تنخفض من 58.05 إلى 49.6 مع مادة بولى إيثيلين جليكول 600 داى – أولييت وإلى49.13 داين سم$^{-1}$ مع مادة توب فيلم. معاملات المستحلب نجحت فى إختبار ثبات المستحلب حسب المواصفات المعروفة للمستحلب.

3 – عند خلط مستحلب الكلوربيريفوس مع عامل الإستحلاب بولى أوكسى إيثيلين 600 داى – أولييت (0.1 %) ينتج عنه زيادة جوهرية من ناحية الفاعلية ضد ديدان لوز القطن بإستخدام الجرعة الموصى بها للمبيد ولاتختلف النتيجة عما سبق بالنسبة لمبيد السيبرمثرين.

4 – بإستخدام طريقة التغذية على أوراق الخس المرشوشة حقليا بمبيد كلوربيريفوس وجد أن الخلط مع المادة النشطة سطحيا تزيد سميتة ضد قوقع الحدائق البنى (أيوبانيا فيرميكيولاتا) وقوقع الحدائق الصغير (تيبا بيسانا) حتى 15 يوما من التقييم.

عموما فإن فاعلية المبيدات فى صورة المركزات القابلة للإستحلاب يمكن زيادة فعاليتها ضد الأفات عند خلطها مع مادة نشطة سطحيا تحسن خواص التبليل والإنتشار على الأسطح النباتية المرشوشة.